

# Mg/Sr distribution and diagenesis of Maastrichtian white chalk and Danian bryozoan limestone from Jylland, Denmark

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The section of 40 m Maastrichtian white chalk and Danian bryozoan limestone at 'Dania' cement works, Assens, Jylland, is described with respect to microstructures, diagenetic features and distribution of magnesium and strontium. The sediments are predominantly composed of biogenic constituents. The Maastrichtian sediment types (soft white chalk, argillaceous chalk and the hardened limestone of a hardground) are classified as pelagic sediments that owe their present characteristics to the influence of diagenetic processes on a primary unconsolidated coccolith lime mud. The Danian bryozoan limestone is predominantly composed of benthic skeletal organisms.

The magnesium and strontium contents of bulk samples and of skeletal carbonate from a few invertebrate taxa were determined by use of atomic absorption spectrophotometry. The magnesium concentration varies considerably but shows a general increase upwards through the section, ranging from 1300 ppm to 4250 ppm. The strontium curve is straight, ranging within 450–1100 ppm and decreases from the base to the top of the section. Thus the distribution of the two elements shows a significant negative correlation. Furthermore, the insoluble residue of the sediments is positively correlated with the magnesium content.

Three zones are established on the basis of the distribution of magnesium and strontium and the Sr/Mg ratio in the studied section.

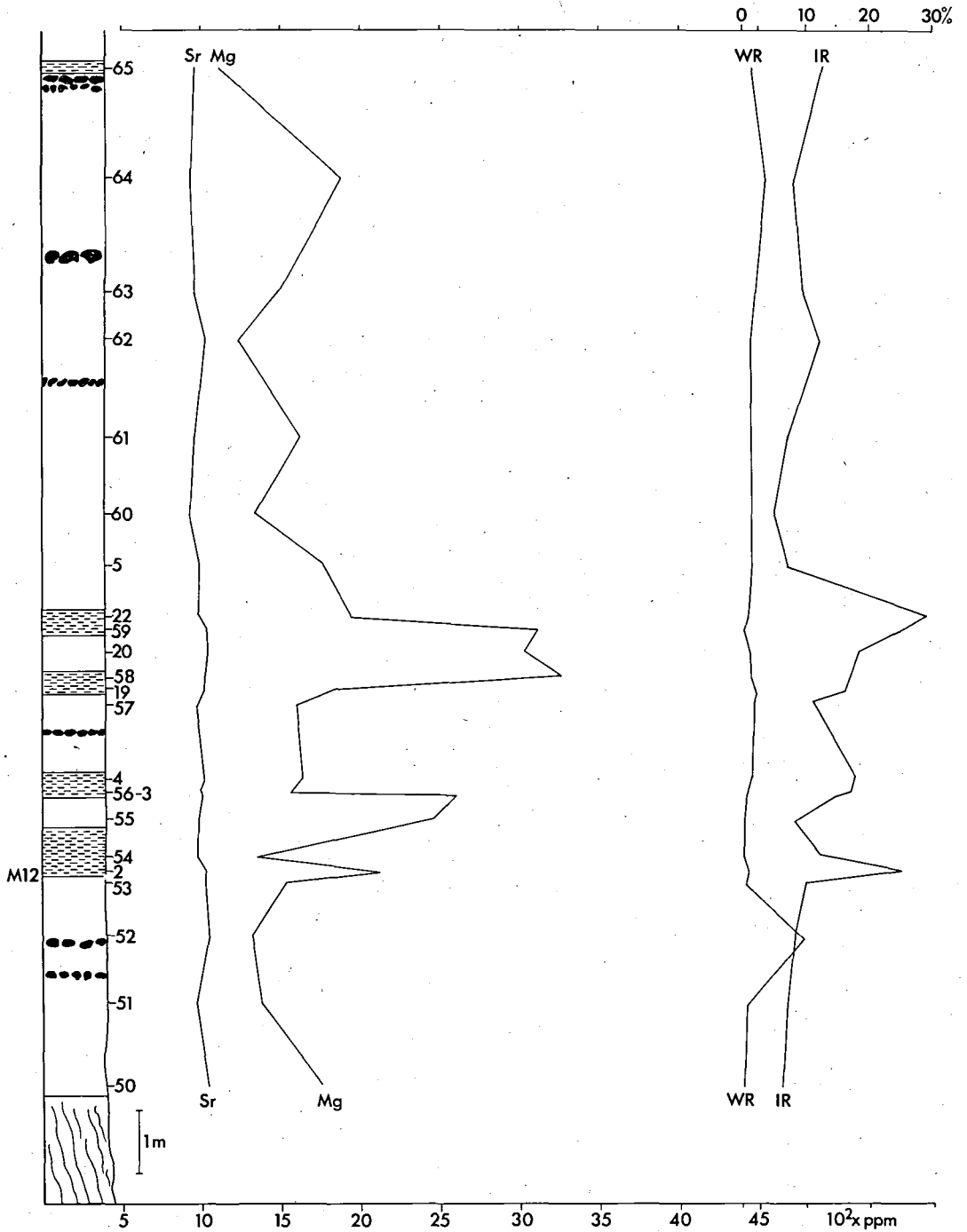
The magnesium and strontium contents of the bulk samples and the individual skeletons are discussed in the light of known factors and processes involved in carbonate biomineralogy. It is stressed that the main factor determining the Sr/Mg ratio is the original aragonite/calcite ratio in the carbonate constituents of the sediments. The variations of the two elements expressed by the negative correlation and the decrease of the Sr/Mg ratio up through the section are believed to be controlled by increasing temperature conditions in the sea where the sediments were deposited. The temperature rise is most likely a function of general climatic conditions and the regression tendencies in late Maastrichtian. Second to temperature, ion-exchange processes may have an influence on the local variations of the Sr/Mg ratio.

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The limestone quarry of Dania Cement Works is located at Assens, 7 km east of Mariager on the southern shore of Mariager Fjord, Jylland (fig. 1). The Danian bryozoan limestone and Maastrichtian white chalk in this area have only a thin Pleistocene cover. The locality has been mentioned many times in the literature e. g., by Grönwall (1900), Ravn (1902, 1903, 1915) Nielsen (1909) and Ødum (1922, 1926). More recent investigations have been carried out by Troelsen (1937, 1955), Wind (1953, 1954) Birkelund (1957) Ødum (1966) and Surlyk (1972). The section now exposed in the 'Dania' quarry consists of approximately 30 m Upper Maastrichtian white chalk with flint layers and argillaceous

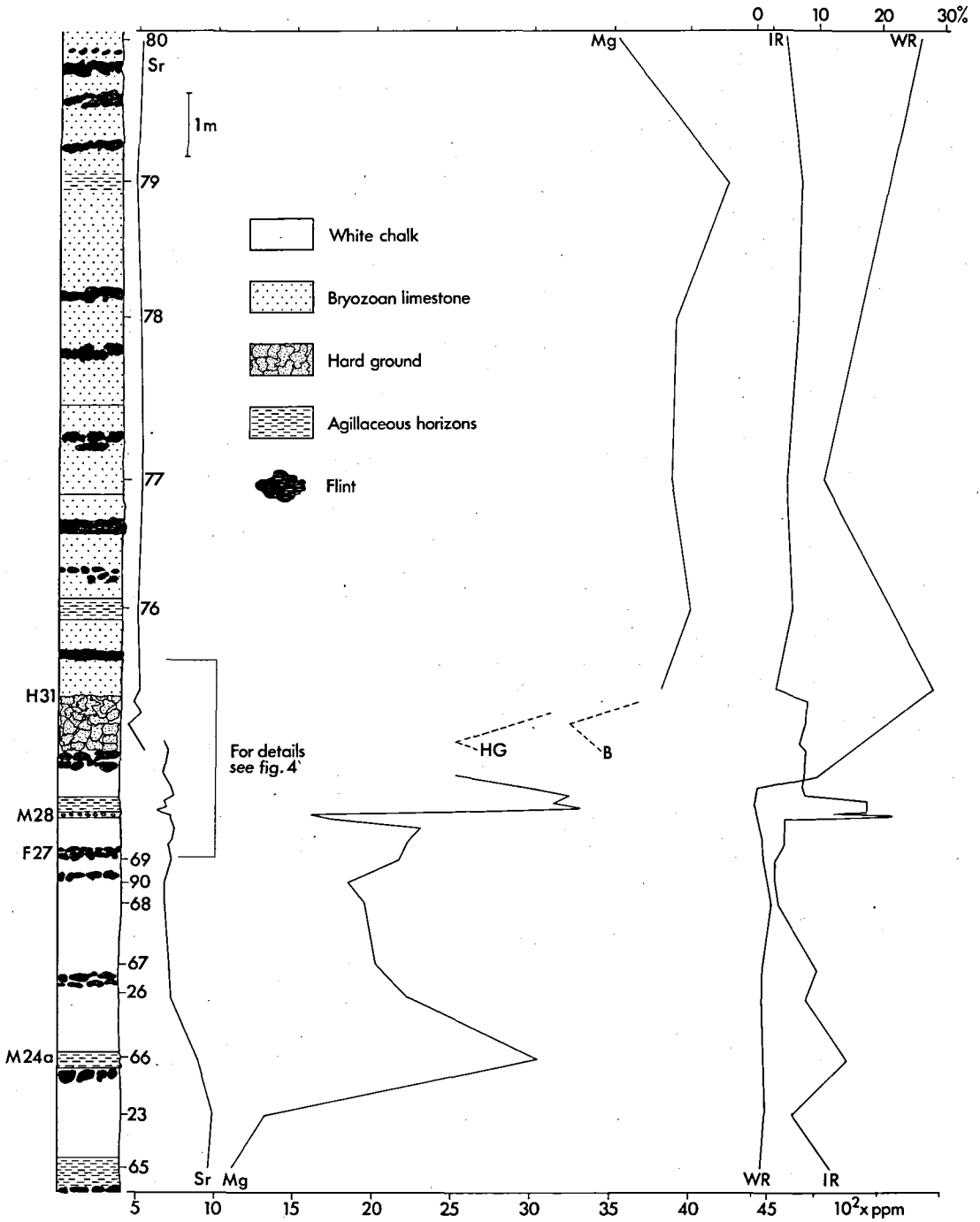
horizons followed by a maximum of 10 m Danian bryozoan limestone, also containing flint. The argillaceous horizons have received attention in the past. They were mentioned by Troelsen (1937) as Cumula clay, by Wind (1954) as blue chalk and as Kjølbygaard Marl by Troelsen (1955).

The present investigation concerns the physicochemical conditions in the sea in which the sediments were deposited and the subsequent diagenetic processes that have affected those sediments. For this purpose a study has been carried out on the grain composition, microstructures, and distribution of magnesium and strontium.



Figs 2-3. Idealized lithological section of the exposed sediments from 'Dania' cement works and the distribution of the belonging contents of Mg, Sr, insoluble residue (IR) and wash residue (WR). HG: Mg values obtained from the indurated limestone of the hard-ground. B: Mg values obtained from the soft infillings

of the burrows in the hardground. The numbers on the right side of the column are sample numbers; marker horizons mentioned in the text are shown on the left. The section was measured by F. Surlyk and E. Håkansson.



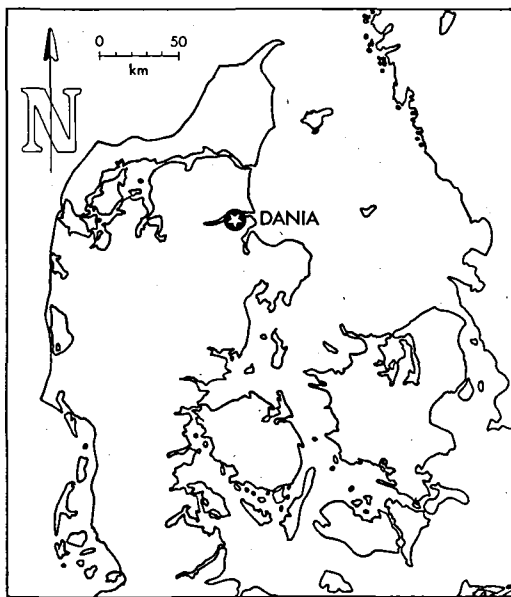


Fig. 1. Map of Denmark showing the location of 'Dania' cement works.

## Stratigraphy

The stratigraphy of 'Dania' is shown diagrammatically in figs 2–4.

The lowermost 3–4 m of the section up to the argillaceous horizon M12 consists of soft white chalk with a uniform appearance. The chalk is interrupted only by two flint layers and burrows are indistinct.

The intermediate part of the section, including the argillaceous horizon M12 and the flint layer F27, is characterized by fluctuation in the amount of insoluble residue varying within 5–30 wt%. In the field this is recorded by the appearance of several grey to grey-brown argillaceous horizons up to 0.75 m thick. Flint layers and nodules are common and burrows are visible throughout all these beds, including different types of *Zoophycos* and *Chondrites* (R. Bromley, pers. comm.).

The Maastrichtian/Danian boundary lies within the sequence between the flint layers F27 and F32 (fig. 4). The most prominent features in the sequence are the marl bed and the hardground. The marl bed is 10–15 cm thick and contains in the lower part a considerable number of 0.25–2 cm angular chalk clasts. The hardground is approximately 0.75 m thick and consists of well-cemented chalk

which is penetrated by a dense tangle of *Thalasinoides* burrows. The upper surface of the indurated bed has a discontinuous lining of glauconite.

Above the hardground the section continues with c. 10 m uniform Danian bryozoan limestone consisting of greyish limestone beds interbedded with several flint layers and indistinct argillaceous horizons. The bryozoan limestone is capped in turn by 2–3 m Pleistocene moraines and soil. The contacts between the moraines and the limestone show small scale karst features like sink holes. Bedding is horizontal throughout the section.

Recent investigations show that the white chalk biostratigraphically belongs to the Upper Maastrichtian *Belemnella casimirovensis* zone (Birkelund, 1957) and to brachiopod zone 10 (Surlyk, 1972) which represent the youngest Maastrichtian exposed in Denmark. The bryozoan limestone is correlated to the two lower Danian biozones of *Tylocidaris oedumi* and *T. abildgaardi*.

The precise level of the Maastrichtian/Danian boundary has not yet been established at the present locality. The most important change in biofacies and lithology is found at the transition from the white chalk to the bryozoan limestone at the top of the hardground. This facies change, however, does not alone define the Maastrichtian/Danian boundary; the boundary sequence at Stevns Klint, for example, is far more complex (Rosenkrantz, 1966). The distribution of dinoflagellates' resting spores indicates that the marl bed (M28) in the section of 'Dania' probably is equivalent to the 'Fiskeler' in the Stevns Klint section, which is the lowermost lithological member of the Danian (J. M. Hansen pers. com.). However, the stratigraphical level of the chalk bed between the marl bed and the hardground at 'Dania' still remains uncertain.

## Material and methods

The present material includes 53 samples of the different sediment types and facies as well as 20 additional samples at the level of D51 (figs 2–4).

Grain size distribution analyses were carried out by disintegrating the consolidated limestone

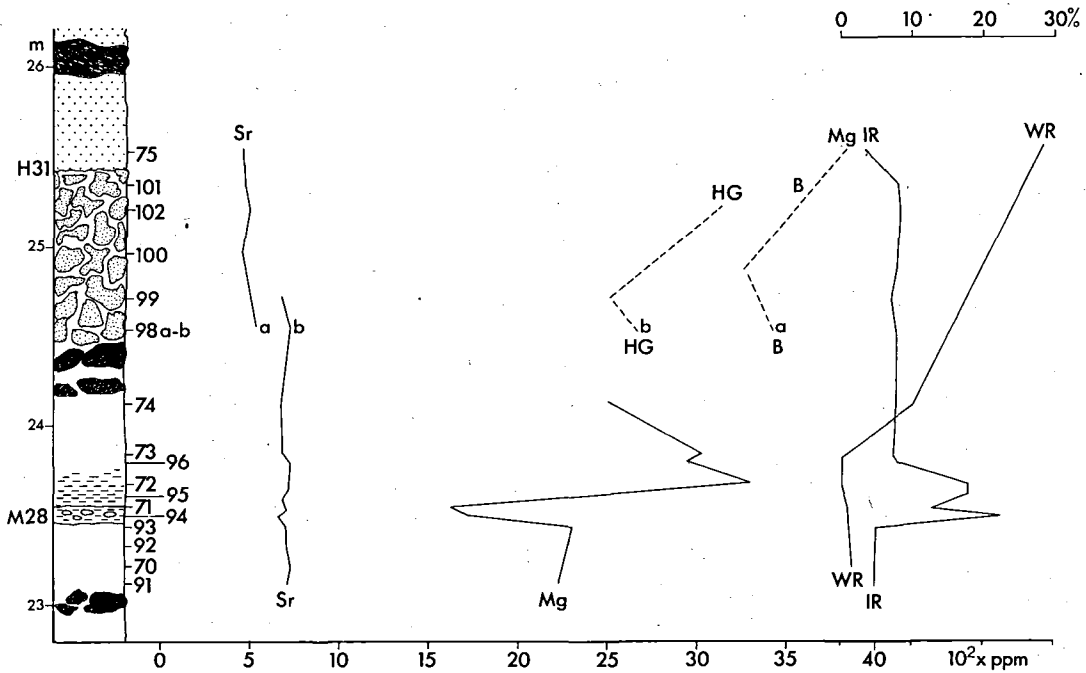


Fig. 4. Detail from figs 2-3 of the Maastrichtian/Danian transition. Legend as in figs 2-3. Sample 98a is from the soft infilling of the burrows in the hardground; sample 98b is taken at the same level but from the indurated limestone of the hardground.

using glauber salt ( $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$ ). The disaggregated sediments were separated into two fractions by use of a  $63 \mu\text{m}$  sieve: Test sieves and gravitational separation were then applied for grain size analyses of coarse and fine fractions respectively. The limestone of the hardground was too indurated for a grain size analysis by this technique. There are many disadvantages inherent in this technique that may lead to errors in the final analysis. Thus, complete disintegration of the samples to the state of original grains of the loose sediment is rarely achieved. This problem is particularly real for grains in the fine silt-clay fraction. Nevertheless, the method is believed to be the most successful technique for getting a fairly reliable impression of the grain size composition of fine grained, slightly consolidated carbonate sediments such as chalk and bryozoan limestone.

Grain identification and grain size analyses were carried out by use of the scanning electron microscope (SEM). The procedure for the

grain size analyses was point counting where the longest visible diameter of the counted grains was measured. A perspex plate with an engraved quadrat net was mounted on the visual recorder of the SEM to ensure a random selection of the counted grains.

The grain composition of the fraction smaller than  $75 \mu\text{m}$  is represented by the percentage relationship between number of coccoliths, invertebrate skeletons and micrite (fig. 6). The amount of insoluble residue (I. R.) was determined by dissolving the carbonate fraction in 10 % HCl.

From parallel samples treated for the purpose of faunistic investigation by the above mentioned disaggregation technique by use of glauber salt it was possible to calculate the weight percent of the wash residue (W. R.) i. e. the grain fraction larger than  $75 \mu\text{m}$ . The W. R. consists predominantly of skeletal fragments and is therefore a relatively good indication for the quantity of invertebrate skeletons in the sediments.

The microstructures of the sediments were studied by the SEM on specimens with fresh fractures and etched surfaces. Two-stage replicas of polished and etched sections of the indurated limestone of the hardground were examined in transmission electron microscope (TEM). Etching was carried out by use of a saturated solution of EDTA for 20 seconds.

The magnesium and strontium contents were determined by use of atomic absorption spectrophotometry. The instrument employed was a Perkin-Elmer Atomic Absorption Spectrophotometer model 303. In addition to the bulk samples, several invertebrate skeletal carbonates were analysed. The preparation of the sample solutions and proper standards was carried out in accordance with normal procedure for determination of elements in the carbonate fraction of limestones (Angino & Billings, 1967). The measurement technique applied was the two-standard method, and the reproductibility is estimated to 3 %.

## The carbonate sediments

The constituents of the carbonate sediments at 'Dania' can be divided into five groups:

1. Carbonate matrix.
2. Carbonate skeletons and shell debris.
3. Carbonate cement.
4. Quartz (detrital, biogenic and authigenic).
5. Associated components (clay minerals, pyrite etc.).

The non-carbonate components play only a limited role in comparison to the total sediment mass, and the present study only deals with the carbonate elements.

Four types of carbonate sediments are distinguished in the section on the basis of grain size distribution, grain component analyses of the fraction  $< 75 \mu\text{m}$ , the quantity of I. R. and microstructures of the sediments; these are: (1) white chalk, (2) argillaceous chalk, (3) indurated limestone of the hardground and (4) the bryozoan limestone.

The sediments have several features in common such as the high carbonate content (70–95 wt%) and a very uniform texture

and fabric. In a wide sense the chalks and the bryozoan limestone consist of a quantity of carbonate skeletons set in a micritic matrix. The fabric of the indurated limestone of the hardground is somewhat different owing to considerable diagenetic alteration.

### White chalk

The white chalk is a consolidated and soft, extremely pure carbonate sediment predominantly composed of grains in the silt-clay fraction (fig. 5). The mean grain size is approximately  $10 \mu\text{m}$  and the amount of insoluble residue ranges between 3.5 and 15 wt%

SEM reveals a fabric of sparse skeletons and skeletal remains within a mosaic of micrite matrix (figs 9–13). The shape of the micritic grains varies from subrounded to irregular. Frequently clusters of coherent micritic grains are observed in the size of 5–15  $\mu\text{m}$  having the appearance of microlumps, occasionally including coccolith fragments.

The skeleton/matrix ratio is in the range  $1/5$ – $1/6$  (figs 2–3, 6). Grains larger than  $10 \mu\text{m}$  generally can be identified as skeletons or shell fragments. Most common are coccoliths and coccolith fragments, which constitute almost the entire part of the grains identified as skeletal in the fraction smaller than  $20 \mu\text{m}$ . The most important invertebrate taxa order of decreasing frequency, are foraminifera, ostracodes, bryozoans, brachiopods and echinoderms. In general the skeletons are well preserved externally, but recrystallization of the original skeletal microstructures has commonly taken place.

The invertebrate skeletons and coccoliths are randomly orientated. Coccoliths show locally abundant concentrations in the sediment.

No calcite cement can be detected within the original pore space. Calcite crystal growth is only observed in connection with the surfaces of the skeletons; in particular a geopetal growth of syntaxial cement is commonly found within foraminiferal chambers (fig. 11). The stereome system of echinoderm plates is consistently filled in with syntaxial cement. In contrast, overgrowth on coccoliths and single coccolith plates rarely is observed. Uncommonly, isolated single euhedral crystals

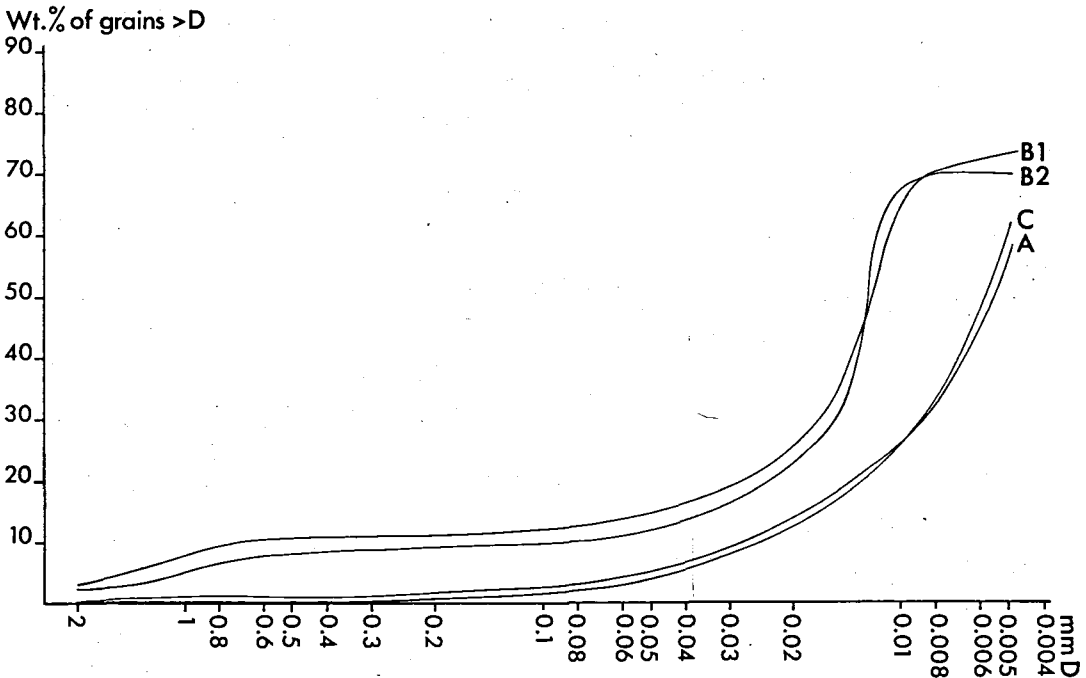


Fig. 5. Grain size distribution of different sediment types. A: argillaceous chalk, sample 59. B1 & B2: bryozoan limestone, samples 76 and 78 respectively. C: white chalk, sample 68.

occur showing no obvious relationship to the surrounding grains (fig. 12). Spherulitic aggregates much like the lepidospheres described by Weaver & Wise (1972) and Scholle (1974) are commonly observed and may be present in large numbers, even in small areas of the samples (fig. 12).

Despite some recognizable variation in the amount and quality of the skeletal components and the content of the insoluble residue the general impression of the white chalk is that of an extremely homogenous biomicrite.

#### Argillaceous chalk

The term 'argillaceous chalk' is used here to characterize chalk containing 15–30 wt% insoluble residue. A gradual transition from 'normal' white chalk into argillaceous chalk is found, but the boundary is placed at 15 wt% because chalk containing more than 15 wt% insoluble residue gains of greyish to brownish colour which makes it easily distinguishable from the white chalk in the field. Argillaceous chalk generally is found in well defined beds seldom more than 0.75 m thick.

Argillaceous chalk shows strong affinities to white chalk; the mean grain size and the grain composition are almost identical (figs. 5, 14–15). But they differ in several important respects. In addition to the considerably higher content of clastic material in the form of clay minerals, there is also a slight but significant increase in the amount of skeletal grains, especially the number of coccoliths (fig. 6). This is reflected in increasing skeleton/matrix ratio up to approximately  $1/4$ . Furthermore, the skeletons exhibit a better state of external preservation i. e. they seem to be 'cleaner', and microlumps such as are found in the white chalk are very seldom observed. It is generally stated that the consolidation of the sediment is much less advanced in comparison to the white chalk. However, the diagenetic phenomena observed in the white chalk are also found in the argillaceous chalk. Most skeletal structures are recrystallized and calcite cement is found as syntaxial overgrowth on the inner surfaces of the skeletons and filling the stereome systems of echinoderms.

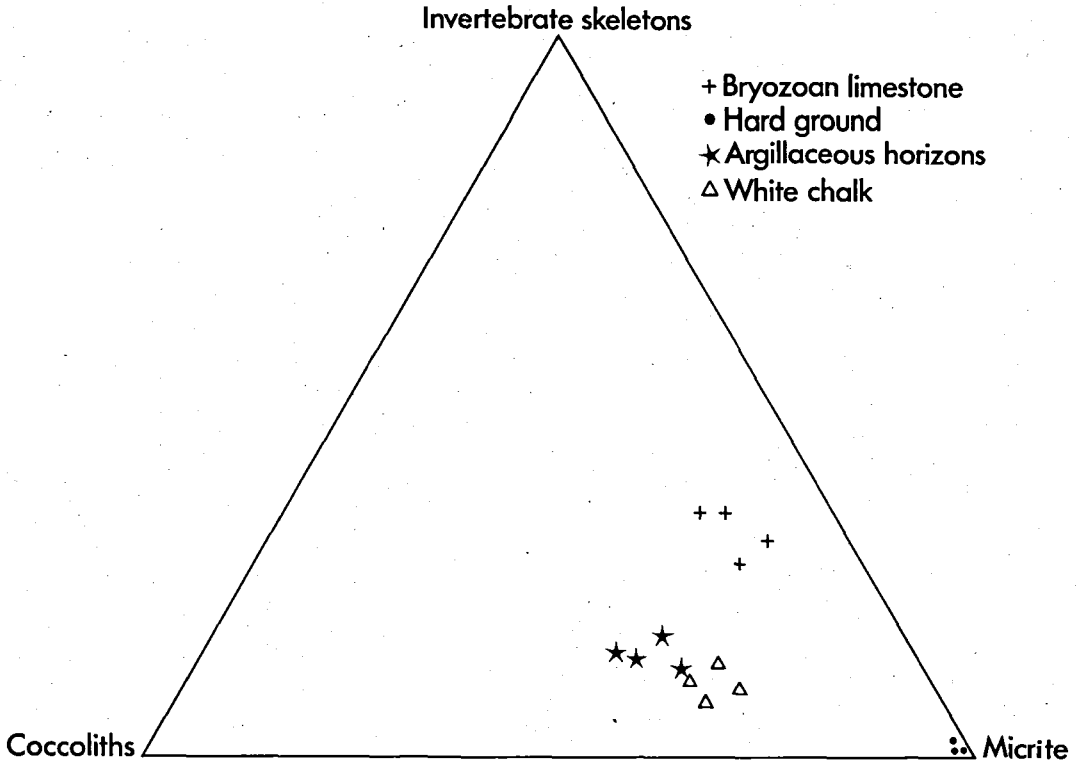


Fig. 6. The percentage relationship between number of invertebrate skeletons, coccoliths and micrite in the grain size interval  $<75 \mu\text{m}$  of the different sediment types.

The indurated limestone of the hardground

The hardground limestone is pale yellow and well cemented with a grain size composition in the silt-clay fraction. The insoluble residue is in the same order of size as those of the white chalk and bryozoan limestone (i. e. c. 8 wt%).

The cementation of the sediment has reduced the original pore volume considerably but the limestone still retains a significant intercrystalline porosity. The cementation is most advanced in the top of the hardground, whereas partial cementation is found in the lower part of the bed (figs 16–26).

Two essentially different fabrics have been found in the limestone: (1) a mosaic of interlocking microspar and micritic grains (the term 'microspar' is here applied for calcite cement with crystal sizes  $< 4 \mu\text{m}$ ) and (2) void-filling sparry calcite cement.

The mosaic of interlocking microspar and micritic grains is the dominant fabric of the

limestone (figs 16, 20, 23). The majority of the grains have a maximum diameter in the range of  $0.5\text{--}5 \mu\text{m}$  and point counting reveals an extreme uniformity of grain size in comparison with the other investigated sediments (fig. 7). In sections the outlines of the grains are rather irregular; plane crystal interfaces and enfacial junctions are seldom observed (figs 19–20). Fracture surfaces show only sparse crystal faces in the grain fraction smaller than  $4 \mu\text{m}$  (fig. 23). It is difficult to distinguish between microspar and the original micritic grains, except where a rare crystal face is found disclosing the presence of microspar.

The relationship between microspar and the original micritic grains can be most clearly seen in the partially cemented patches in the lower part of the bed. The calcite crystals of the cement are here somewhat larger ( $3\text{--}8 \mu\text{m}$  in diameter) in comparison with the microspar of the well-cemented part of the hardground.



Table 1. Obtained values for magnesium, strontium and insoluble residue of 20 samples from the level of sample 51.  $\bar{x}$ : arithmetic mean.  $s$ : calculated standard deviation.

Sample	Mg ppm	Sr ppm	IR %
D51 - 1	1356	927	7.4
2	1326	918	6.9
3	1392	945	5.9
4	1404	940	6.2
5	1410	939	6.4
6	1368	930	6.4
7	1398	922	6.8
8	1338	941	6.9
9	1408	920	6.3
10	1385	917	6.4
11	1363	928	6.7
12	1395	948	7.1
13	1401	933	7.0
14	1379	937	6.8
15	1384	939	6.3
16	1392	943	6.0
17	1373	940	6.9
18	1389	935	7.0
19	1348	948	6.1
20	1350	931	6.3
	$\bar{x} = 1378$ $s = 24$	$\bar{x} = 934$ $s = 10$	$\bar{x} = 6.6$ $s = 0.7$

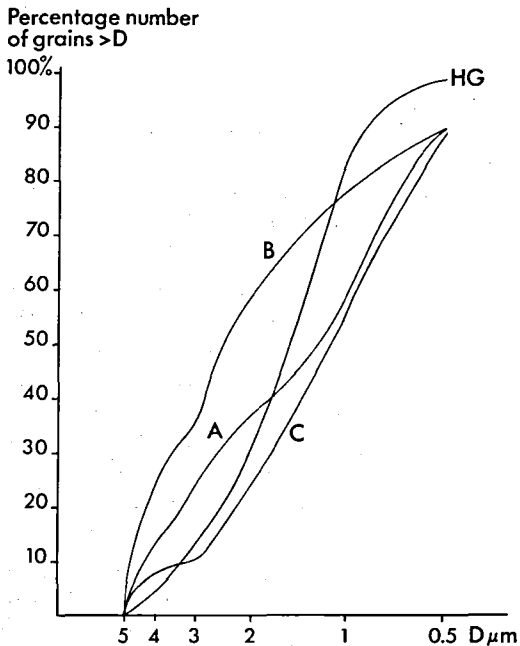


Fig. 7. Grain size distribution on basis of point counting (SEM) in the grain size interval  $< 5 \mu\text{m}$ . A: argillaceous chalk. B: bryozoan limestone. C: white chalk. HG: the indurated limestone of the hardground.

An extensive consumption of micrite has taken place by enclosure of the micritic grains within the sparry calcite crystals (figs 25–26). It is impossible to tell if syntaxial growth or simple overgrowth are involved but most likely both types of processes have been active.

Preserved skeletons and skeletal remains are extremely rare (fig. 6), and of them coccoliths and coccolith fragments are observed most frequently (figs 21–22). However, an originally large content of skeletal components, comparable with that of the chalk, is indicated by abundant moulds of 'calcspheres' and foraminiferal tests (figs 16, 18). Furthermore there are large quantities of skeletons in the partially cemented parts of the bed (fig. 24). Skeletal structures are seen in sections as oriented and otherwise organized crystals, completely enveloped by matrix (fig. 19). The interfaces between organized skeletal structures and matrix often show a ragged and blurred appearance indicating advancing 'micritization' i.e. advancing transformation of ordered crystalline structures into uniform micritic mosaic. The coccoliths seem to have disintegrated in the same manner (figs 21–22). This process is most advanced towards the top of the hardground.

Voids are completely or partially filled in with sparry calcite cement (figs 17–18). Some of the voids are evidently external moulds after dissolved skeletons. Crystal faces are developed within remaining pore space (fig. 17). The most common crystal faces seen are positive and/or negative rhombohedrons. The longest diameter of the crystals may vary within 5–50  $\mu\text{m}$  and there is a preferred orientation of the longest axes towards the centre of the void.

Calcite cement is also found in the form of syntaxial growth on skeletal surfaces. However, the skeletons themselves are normally 'micritized' and the syntaxial cement remains as a mould that reveals the former presence of skeletal fragments (figs 19, 21).

#### Bryozoan limestone

The Danian bryozoan limestone differs in many respects from the carbonate sediments in the chalk sequence and introduces a facies shift in the section studied. The limestone is

a white to greyish, slightly consolidated, porous carbonate sediment predominantly composed of grains in the silt fraction (fig. 5). The mean grain size is approximately 30  $\mu\text{m}$  and thus is considerably coarser than the sediments in the chalk sequence. The coarseness of the bryozoan limestone is caused by a great increase in the number of invertebrate skeletal components reaching 10–25 wt% in wash residues. Bryozoan zoaria and fragments are the dominant grain type in the fraction  $> 75 \mu\text{m}$ .

The increased content of skeletal components also has its effect on the grain composition of the silt-clay fraction (fig. 7). Coccoliths and planktic foraminifera are not as frequent in this fraction in comparison to the chalks. In contrast, other types of skeletons, especially minute bryozoan fragments and 'calci-spheres' show an increase in number, which is reflected in a skeleton/matrix ratio as high as  $1/1$ .

The amount of insoluble residue is quite constant, ranging within 4–8 wt%, which is the same order of size as the values for the white chalk.

The fabric of the bryozoan limestone is quite similar to that of the chalk, although grain size and grain composition are somewhat different (figs 28–30). The matrix consists of subrounded to irregular grains structurally very much resembling the matrix of the chalks. The skeletal grains show random orientation. Calcite cement is only found as syntaxial overgrowth on skeletal surfaces (fig. 32) and recrystallization of skeletal structures is throughout a common phenomenon (fig. 31). Micro-lumps, i. e. 5–20  $\mu\text{m}$  aggregates of micritic grains are abundant and may be isolated (fig. 27) or welded to the surfaces of the skeletons.

### Distribution of magnesium and strontium

The general trend of the curves illustrated in figs 2–4 exhibits a great variation of the Mg and Sr content in the section studied.

In order to study the lateral variation and hereby test the reliability of the vertical distribution, 20 samples from level D51 were col-

lected over a distance of about 200 m along the section. The samples were analysed for the content of magnesium and strontium and the amount of insoluble residue. The results are recorded in table 1 together with the calculated means and standard deviations. A computation of  $\chi^2$  was carried out on the present data and values of  $P_c$  were obtained in the interval of 0.30–0.50 for all three populations, which is considered to indicate satisfactory normal distribution of the observations. While so few as 20 observations renders a  $\chi^2$  test of doubtful value, nevertheless, by comparing the  $P_c$  values, the calculated standard deviations and the obtained data from the vertical section (table 2), the bulk samples may be considered to give fairly representative values for the individual stratigraphical horizons.

Table 1 illustrates the remarkable difference in distribution of Mg and Sr. Although the values for both Mg and Sr concentrations are in the same order of size ( $10^3$  ppm), the standard deviation for Mg is 2.5 times that calculated for Sr, demonstrating that the variation of the Mg content is much larger than in the case of Sr. The phenomenon is also reflected by the curves in figs 2–4. The Sr content is characterized by a relatively straight progress, whereas the Mg curve shows much greater swings and may vary several hundred ppm in a sequence of a few metres.

The strontium content decreases from 1100 ppm to c. 450 ppm and the magnesium content increases from c. 1300 ppm to c. 4250 ppm from base to top of the section. This negative correlation is most pronounced in the chalk sequence whereas the concentrations of the two elements in the bryozoan limestone seem to have reached stability; the distribution trends here are nevertheless in good agreement with the values obtained from the chalk.

All evidence indicates a positive correlation between magnesium content and the insoluble residue. The Mg content increases by up to 1500 ppm in the argillaceous horizons. In contrast, the strontium content does not show any correlation with the insoluble residue.

The large wash residue of the bryozoan limestone coincides with the minimum and maximum values for Sr and Mg respectively,

Table 2. Values for magnesium, strontium, wash residue, insoluble residue and the Sr/Mg ratio from bulk samples.

Sample	Mg ppm	Sr ppm	W.R. %	I.R. %	Sr/Mg
D80	3525	525	26.0	4.8	0.1
D79	4222	516	-	7.2	0.1
D78	3892	528	-	6.6	0.1
D77	3866	502	10.7	4.9	0.1
D76	3994	492	-	5.6	0.1
D75	3818	454	28.2	3.3	0.1
D101	3656	473	-	8.0	0.1
D102	3118	496	-	8.2	0.2
D100	3243	463	-	8.2	0.1
D99	2517	670	-	7.2	0.3
D98a	2658	524	-	7.8	0.2
D98b	3422	718	-	8.0	0.2
D74	2508	686	10.0	7.8	0.3
D73	3018	698	0.3	7.5	0.2
D96	2948	719	-	7.8	0.2
D72	3307	708	0.1	17.8	0.2
D95	2515	695	-	17.6	0.3
D71	1618	706	0.7	12.8	0.4
D94	1710	668	-	22.2	0.4
D93	2296	701	-	5.1	0.3
D92	2267	708	-	5.0	0.3
D70	2245	726	1.5	4.9	0.3
D91	2218	710	-	4.9	0.3
D69	2185	723	1.8	3.6	0.3
D90	1832	686	-	3.5	0.4
D68	1945	675	2.7	3.8	0.3
D67	2017	703	1.6	10.2	0.3
D26	2225	722	1.4	8.1	0.3
D66	3036	879	-	14.9	0.3
D23	1308	985	2.0	6.4	0.8
D65	1113	972	1.4	12.5	0.9
D64	1898	937	3.4	8.0	0.5
D63	1495	963	-	9.3	0.6
D62	1240	1034	1.3	11.9	0.8
D61	1608	972	-	6.8	0.6
D60	1337	929	-	4.9	0.7
D5	1766	995	1.2	6.9	0.6
D22	1947	981	1.6	28.7	0.5
D59	3118	1026	0.2	24.3	0.3
D20	3022	1032	1.1	17.8	0.3
D58	3238	1020	1.2	16.8	0.3
D19	1838	1011	2.0	17.5	0.6
D57	1602	985	2.8	10.9	0.6
D4	1623	1019	1.4	17.6	0.6
D56	1566	1003	0.4	16.9	0.6
D3	2605	1010	0.6	14.6	0.4
D55	2458	992	0.2	8.1	0.4
D54	1318	989	0.2	12.3	0.8
D2	2117	1021	0.8	24.8	0.5
D53	1536	1016	0.5	9.9	0.7
D52	1327	1069	9.5	8.3	0.8
D51	1368	979	0.5	6.8	0.7
D50	1749	1048	0.2	6.1	0.6

but a detailed examination of the curves reveals no correlation between the striking swings of the elemental concentrations and the contents of larger invertebrate skeletons, represented by the size of the wash residue.

Neither has any correlation been found between wash residue and insoluble residue.

The concentrations of Mg and Sr were specially analysed in carbonate skeletons of a few invertebrate taxa from selected levels in the section and compared with the corresponding values from the bulk samples for the purpose of obtaining more precise information on the placing and distribution of the two elements. The invertebrate skeletons analysed were echinoid plates (*Tylocidaris* spp.) bryozoan zoaria, different benthic foraminifera and an ostracode (*Bairdia denticulata*). It is emphasized that the skeletons were collected from samples disintegrated by use of glauher salt, and the samples have therefore been treated extremely rigorously in comparison to normal preparation procedure for trace element analyses. Nevertheless, the obtained results seem credible, even though non-controllable uncertainties may be involved (fig. 8a-b).

The general shape of the curves is subparallel to those of the bulk samples, and confirms the negative correlation between the two elements. Thus a high Mg content corresponds with relatively low Sr content (most striking by comparing the contents in the bryozoan skeletons and the foraminiferal tests). The echinoid plates, which contain a considerable amount of syntaxial cement, nevertheless show a similar distribution pattern for the two elements as bulk samples and the other skeletons analysed.

With a few exceptions the Mg content in the chalk sequence is higher in the carbonate skeletons than in the corresponding bulk samples, whereas the opposite is the case in the bryozoan limestone. However, the great increase of the Mg content in the argillaceous horizon (sample D59) is not reflected in the Mg content found in the carbonate skeletons.

On the other hand, the Sr content of the bulk samples is generally significantly higher than the concentrations found in the carbonate skeleton in both the chalk sediments and the bryozoan limestone. Only the values for the benthic foraminifera come close to the curve of the bulk samples. But it is worthwhile noting that the differences between the Sr content of bulk samples and carbonate skeletons de-

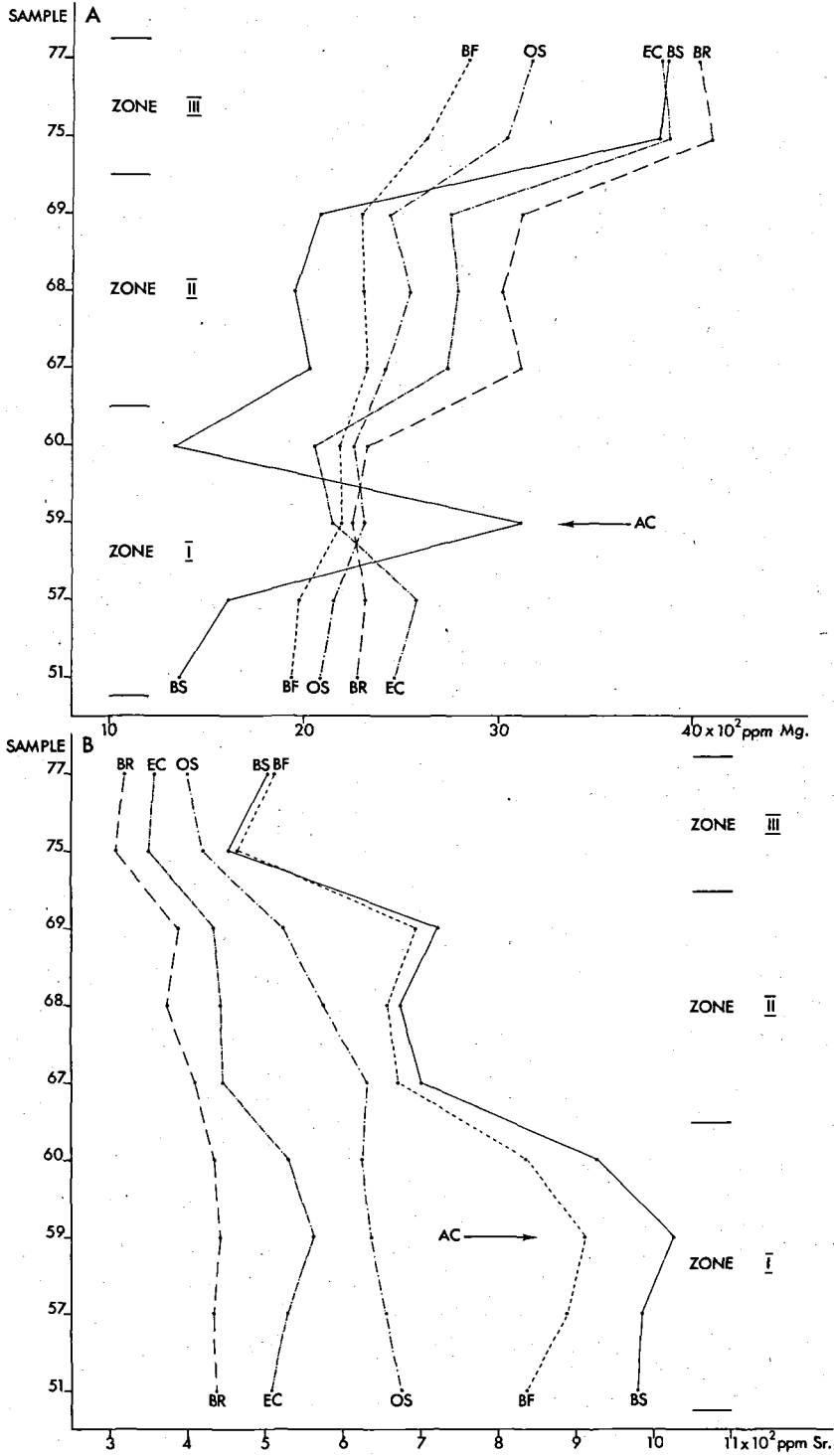


Fig. 8a-b. The distribution of magnesium (A) and strontium (B) in selected bulk samples and the invertebrate skeletons in each. BS: bulk sample. BF: benthic foraminifera. BR: bryozoans. EC: echinoderms. OS: ostracodes. AC: sample 59 (argillaceous chalk).

crease simultaneously with the decrease of the absolute values up through the section.

The present distribution of the Mg and Sr contents makes it possible to establish three zones in the section studied. The extremely high concentrations of Mg in the argillaceous horizons are believed to be caused by physical properties of the present clay minerals and consequently are not taken into account in determination of the zonation.

*Zone I* consists of the lowermost part of the section including the argillaceous horizon at M24 and sample D23 (figs 2–3). The zone contains some of the most pronounced argillaceous horizons in the section and sequences with a large number of different burrows, as well as homogeneous white chalk. In this zone the average Sr/Mg ratio is 0.7. Despite the heterogeneous lithology the Sr content shows a remarkably constant level in the range of 850–1060 ppm but slightly decreasing from base to top of the zone. The Mg content varies from 1250 ppm to about 2000 ppm.

*Zone II* includes the uppermost part of the Maastrichtian strata and the main part of the Maastrichtian/Danian boundary sequence i. e. from sample D23 up to the lower part of the hardground. The average Sr/Mg ratio of the zone is 0.3. Only 4 m thick, the zone contains several lithological units and diagenetic features like argillaceous horizons, a marl bed, white chalk, a hardground and flint layers. The complex lithological composition reflects the transition of the Maastrichtian/Danian boundary, which terminated the monotonous sedimentological conditions in the Maastrichtian sea.

The Sr content in this part of the section does not, however, reflect these geological events, but keeps throughout a constant level in the range of 650–750 ppm. The Mg concentrations are less constant varying from 1600 ppm to about 2700 ppm.

*Zone III* comprises the Danian bryozoan limestone and exhibits the smallest Sr/Mg ratio in the section studied, c. 0.1. The Sr content ranges within 450–550 ppm, whereas the Mg varies from 3500 ppm to 4250 ppm.

The hardground makes up a transitional sequence between zones II and III (fig. 4). The Sr concentrations recorded in the limestone

clearly stress the relationship to the bryozoan limestone except for the lowermost 20 cm. The Mg content, however, shows intermediate values.

## Discussion and interpretation

The characteristics of the sediments may be divided into primary and secondary features. The primary features are grouped in terms of depositional environments which are essentially twofold: (1) the physical and chemical depositional processes (i. e. the sedimentary facies in wide sense) and (2) the biological aspects in the form of carbonate biomineralogy.

The secondary features have been produced subsequently by processes of diagenesis.

Facies and diagenesis are illustrated by the fabric and the texture of the sediments. The nature of the carbonate biomineralogy has commonly been obscured by subsequent alterations, but may be indicated indirectly by the magnesium and strontium distribution in the carbonate fraction. In the following sections, facies, diagenesis and influence of biomineralogy as expressed by the Mg and Sr content are discussed on the basis of the data from the present sediments.

### Facies

The sediments consist predominantly of carbonate constituents with a minor increase in terrigenous material at argillaceous horizons. The soft sediments show no indications of any primary precipitation of a purely physico-chemical nature. Evidence of syndepositional precipitation of calcium carbonate is seen only at the hardground. Neither have any intraclasts been recorded, except at the hardground. The chalks and the bryozoan limestone are purely biogenic sediments originating from in situ accumulation of carbonate skeletons and consequently the nature of the sediments is dominantly influenced by ecological factors characterized by the configuration of the ecosystem.

Two types of biofacies are recorded in the section on the basis of different modes of life of the rock forming organisms: the pelagic Maastrichtian chalks and the benthic Danian bryozoan limestone.

The white chalk and the argillaceous chalk are typical pelagic sediments predominantly composed of skeletons of coccolithophorids and planktic foraminifera. The hardground naturally attaches itself to this group through grain size distribution and skeletal content. Skeletons of benthos in the chalk sediments make up less than 5 wt% and are insignificant as rock building components.

Estimates of the depositional depth for the Maastrichtian chalk have been based chiefly on comparative studies of fossil assemblages and their recent relatives. Such studies have indicated a depositional depth in the range of 100–250 m, corresponding to outer shelf environments (Nestler, 1965; Håkansson et al., 1974).

The bryozoan limestone introduces a new biofacies in which benthic sessile invertebrates, predominantly bryozoans, appear as the most important rock forming organisms. The environmental change that altered the ecosystem most likely was due to the regression in late Maastrichtian and Danian time (Håkansson et al., 1974). However, the lithological alteration is remarkably faint. The carbonate fraction still amounts to  $> 90$  wt% and it is emphasized that although larger invertebrate skeletons characterize the limestone, they never exceed 30 wt% of the total sediment mass. The silt-clay fraction still forms the most important constituents of the sediment.

The bryozoan zoaria and other skeletons do not show any preferred orientation and have most likely accumulated in situ. The inhomogeneous grain size composition indicates a low depositional energy level; although the deposition of the bryozoan limestone probably occurred in a shallower sea than the Maastrichtian chalks, the sediment displays no tangible near-shore or littoral features.

#### Diagenesis

A remarkable feature for both the chalks and the Danian bryozoan limestone is that bedding, grain orientation and other primary sedimentary structures are almost lacking or blurred. The extremely homogeneous structural appearance is probably the result of intensive bioturbation. Bioturbation, passage through sediment-eaters' intestines and the activity of

boring organisms most likely also caused the abrasion and mechanical break down of the skeletal units which is reflected in the over all dominance of micritic grains.

The soft chalks are relatively unaffected by diagenetic processes in comparison with other ancient carbonate sediments. This is most commonly explained by the dominance in chalks of low Mg calcite in form of coccoliths ( $< 1$  wt%  $MgCO_3$ ; Thompson & Bowen, 1969) so that already in the depositional phase the sediment was in near equilibrium with the physicochemical conditions in the sediment-water interface. Nevertheless, some alterations took place in the early diagenetic stage. Most invertebrate skeletons display some degree of recrystallization, a process that most likely began in the sediment-water interface (Berger 1967, 1972). Aragonite skeletons were completely dissolved, but the former presence of aragonite skeletons is disclosed by moulds in the chalk and the hardground.

The porosity of the soft chalks has been estimated to be in the range of 45–65% (Håkansson et al., 1974; Scholle, 1974). The amount of interstitial cement is insignificant so the reduction of pore volume has been attributed to dewatering and compaction (Håkansson et al., 1974). The compaction is expressed by slightly deformed burrows and crushed macrofossils. Strong deformation is in most cases restricted to beds showing slumping and sediment flow (Surlyk, 1972). In contrast, smaller invertebrates and microfossils with or without infilling of micrite do not demonstrate any deformation (compare Scholle, 1974). The effect of the compaction is therefore remarkably faint.

Consolidation of the soft sediment is most likely due to pressure-solution processes. Neugebauer (1973, 1974) deduced the relationship between such factors as overload, grain contact, stability of the mineral phases and the influence of the magnesium concentration in the pore fluid and applied his results to chalk. He also stressed the small volume of cement produced by the processes involved. However, the minute grain size and grain contacts hinder primary observations and it has therefore not been possible unambiguously to

demonstrate any fabric that has resulted from pressure-solution processes.

While the chalk sequence generally appears to be diagenetically homogeneous, the following succession of increasing degrees of diagenetic alteration can nevertheless be demonstrated: argillaceous chalk – white chalk – hardground.

The argillaceous chalk is the least altered sediment in the section. The sediment has evidently been exposed to the same overload and stress as the white chalk, but there must be a considerable number of grain contacts in the argillaceous chalk between carbonate crystals and clay particles in contrast to the complete dominance of carbonate crystal contacts in the white chalk. The easy disintegration of the argillaceous chalk is therefore explained by reduced coherence of the grains and the ability of the clay minerals to incorporate a considerable amount of water in the crystal lattice by swelling. It is probable that pressure-solution at a clay/carbonate contact produces little or no cement, which may explain the generally smaller quantity of cement in the argillaceous chalk than in the pure chalk. Removal of free ions from the pore fluid by adsorption to clay minerals may also be involved. The present magnesium distribution indicates that a significant ion-exchange has indeed taken place in connection with the clay minerals.

The hardground shows the most interesting and complex features in the section. Hardgrounds are not uncommon in north European chalks (e. g. Voigt, 1959; Bromley, 1975). All lines of evidence suggest a consolidation of the hardground horizon at the sediment-water interface. The cementation is apparently not the result of redistribution of carbonate by leaching or dissolution from the nearby sediments, and the physicochemical processes involved are believed to be precipitation of carbonate cement from the sea water.

In the last decade several examples of recent submarine lithification have been described (review in Bathurst, 1971). Cementation in these cases has been initiated by supersaturation of the interstitial water with respect to magnesian calcite and aragonite. The cement recorded in the present hardground is low

magnesium calcite, but there is nothing to prevent the original cementing minerals having been metastable aragonite and/or magnesian calcite. The present fabric and mineralogy thus resulting from subsequent recrystallization and crystal growth. The strikingly 'well-sorted' appearance of the grain size distribution of the finest fraction in comparison with the other carbonate sediments (fig. 6) shows that the diagenetic processes brought along an equalization of the grain size in the original sediment. The smallest grains have been consumed or locked up by the cement and the larger grains (i. e. predominantly the skeletons) have been 'micritized'. It is difficult to explain the destruction of the skeletal structures in the hardground in contrast to the relatively well-preserved skeletons in the chalks and the bryozoan limestone. However, it is tempting to relate the phenomenon with the chemical progress of precipitation of cement and recrystallization in the hardground even though the processes involved are not understood.

The diagenetic effects on the bryozoan limestone are much the same as those observed in the white chalk. The sediment is lithified to a similar degree, probably again as a result of pressure solution processes. However, the more advanced growth of syntaxial cement and the large number of microlumps indicate a higher primary chemical instability of the sediment in comparison to the white chalk, which is most likely related to the higher content of magnesian calcitic rock forming skeletons.

#### Magnesium and strontium content

Estimation of the significance of the Mg and Sr distribution in carbonate sediments necessarily involves a discussion of the physicochemical and biochemical control of the two elements. A comprehensive summary is given by Dodd (1967), Wolf et al. (1967), Bathurst (1971) and Milliman (1974) and only the most relevant aspect are reviewed in the following paragraphs.

The fact that most marine carbonate sediments predominantly have biogenic origins has resulted in abundant research on the topic of magnesium and strontium distribution in skele-

tal carbonates. Three independent factors influence the biochemistry and composition of skeletons: (1) physicochemical, (2) physiological (genetic) and (3) environmental factors.

The characteristic distribution of magnesium and strontium cations substituting  $\text{Ca}^{2+}$  in the polymorphs of calcium carbonate due to the different crystal lattice configuration has been thoroughly demonstrated in connection with the Mg/Sr ratios in calcitic and aragonitic secreting organisms and the mineralogy is consequently the most important parameter determining the Mg and Sr contents in skeletons and carbonate sediments.

The considerable variation in the magnesium content of calcitic skeletons of different major taxa was earlier attributed to generic control whereas the variable amount of magnesium in the single animal species has been considered to be caused by environmental factors like temperature and salinity. However, recent studies have revealed that the importance of temperature and salinity do not seem to be so unambiguous as first supposed. Poorly understood physiological factors (growth rates and probably the ontogenetic age) have been suggested as being involved, and recent investigations of several invertebrate taxa emphasize this point of view. The variation of the magnesium content in ostracodes (Cadot et al., 1972), echinoids (Sumich & McCauley, 1972), echinoids and asteroids (Weber, 1973) and milionid foraminifera (Ponder & Glendinning, 1974) all show a more complex pattern of the distribution of this element in relation to environmental and physiological factors.

As with magnesium a remarkable stability also of the strontium content has been demonstrated in most studied invertebrate taxa at the class level. A few publications deal with a possible temperature and salinity control within single taxa. Unfortunately the obtained results are rather heterogeneous and they may be obscured by unknown physiological (genetic) parameters. Nevertheless, an inverse relationship between temperature and strontium content has been demonstrated in several instances. Experimental data on the Sr/Mg ratio for inorganic precipitated aragonite, also show a linear inverse correlation to temperature below 100 C° (Kinsmann & Holland, 1969).

It may thus be deduced from the available data that the major trends of magnesium and strontium contents of biogenic carbonates depend on the carbonate mineralogy i. e. the calcite/aragonite ratio. The minor variations in the Mg content within a single taxon are positively correlated to temperature although under indirect influence of poorly known physiological factors. Strontium occurs in largest quantity in aragonite and usually exhibits an inverse relationship to temperature. It is apparently valid for both magnesium and strontium that they have no significant correlation to the minor changes in salinity recorded in normal marine environments. The physicochemical processes and factors involved concerning the incorporation of the two elements into inorganic precipitates of calcium carbonate are well understood, but fundamental problems still exist on the distribution of the two elements in biogenic carbonates. The most pressing of those is the understanding of the physiological processes involved in biomineralization.

Numerous investigations have been carried out on the environmental and diagenetic control of magnesium and strontium in carbonate sedimentary environments but it has been difficult to transform the obtained results into valid and usable generalizations. The majority of the studies deal with the Mg/Sr ratio in relation to the calcite/aragonite transition and with respect to reef carbonates contra basin carbonates. In this connexion several authors have questioned the applicability of the elemental content to facies analysis because of the effect of casual diagenetic alterations. However, concerning diagenetic interpretations the magnesium and strontium contents have been used successfully by e. g. Shearman & Shirmohammadi (1969) and Schneidermann (1970).

A possible climatic influence on the Mg/Ca ratio was found by Veizer & Demovič (1973). In a subsequent paper (Veizer & Demovič, 1974) they demonstrated a significant facies dependence for strontium and established five facies types. The chalks and the bryozoan limestone of the present study are classed as pelagic sediments and organoditrital limestone respectively; but the obtained values of the strontium content are rather high ac-



cording to the classification of Veizer & Demovič (1974), probably as a result of faint diagenetic alteration.

The most comparative investigation in relation to the present study is the work on trace and minor elements in carbonate rocks by Honjo & Tabuchi (1970). Among a large number of limestones from all over the world, they also deal with the Mg and Sr contents in the Maastrichtian/Danian sequence of Stevns Klint, Denmark. The data obtained from this section show the same characteristic negative correlation between the two elements as found in Dania. The same trend is also demonstrated in other Maastrichtian/Danian localities in Jylland (unpublished data) and it is probably a general phenomenon in the uppermost Maastrichtian chalk in Denmark.

The abrupt decline in the Sr/Mg ratio in the transition from chalk to bryozoan limestone is most likely due to the shift of biofacies and hereby the contents of dominating rock forming organisms in this part of the section i. e. the low Mg calcitic coccoliths are replaced by bryozoans and other high Mg calcitic organisms.

However, this explanation is not adequate for the distribution trends within the chalk sequence. The decrease in the Sr/Mg ratio from the base to the top of the chalk sequence is just as significant as the decrease from the topmost part of the chalk into the bryozoan limestone. But in contrast, the grain composition within the chalk sequence is rather monotonous and dominated by two taxa only: the coccoliths and second to them, the planktic foraminifera. Some variations are recorded in the amount of larger invertebrates indicated by the wash residue curve (figs 2-3); but the order of size is quite constant, ranging within 3-8 wt%, which is considered to be an insignificant number and can have no influence on the Sr and Mg distribution. Also the grain composition in the silt clay fraction is rather constant (fig. 6).

It is impossible to estimate the influence of possible aragonitic contributors, although it is believed that a part of the strontium content originated from dissolved aragonitic skeletons and is retained in the sediment by adsorption forces. The relative decline of the strontium

content in bulk samples in comparison to the content in the skeletal calcitic carbonate may indicate an absolute decrease in the number of aragonitic secreting organisms in late Maastrichtian time (fig. 8 b). However, only a minor part of the strontium decrease can be explained in that way. It is therefore suggested that it is not a simple shift of the calcite/aragonite ratio that causes the characteristic distribution of the two elements in the chalk sequence. This conception is furthermore stressed by the subparallel curves for the bulk samples and the skeletal carbonate demonstrated in fig. 8 a-b.

Finally, environmental parameters like salinity and temperature may be considered. The fossil assemblages indicate high marine conditions in the Maastrichtian and Danian seas, and fluctuations in the salinity in open marine environments presumably had only an insignificant influence on the elemental distribution in skeletal carbonates. Consequently a temperature increase in the depositional environments is suggested as the most reasonable interpretation of the regular elemental distribution in the chalk sequence according to the known effect of the physicochemical and physiological influence.

Our present knowledge of climatic conditions in the late Maastrichtian is rather restricted. Comprehensive faunistic studies of numerous invertebrate taxa reveal a temperature increase in the north European late Maastrichtian sea (Voigt, 1964). In contrast, oxygen isotope studies on planktic and benthic foraminifera from deep sea cores show a general world wide temperature decline near the end of the Cretaceous through the Campanian and Maastrichtian (Saito & Donk, 1974; Savin et al., in press). The temperature increase suggested in the present paper is geographically restricted to few localities. Exact values cannot be offered, but taking into account the gradient of the magnesium/temperature curves given by Chave (1954) and the strontium/temperature curve by Hallam & Price (1968) the order of magnitude may be estimated to range within 2-4 C°. An essential part of the temperature increase is certainly explained by the lowering of the sea level due to the late Maastrichtian regression

i. e. the temperature difference between outer and inner shelf environments. But the absolute temperature shift is of course the result of an interplay between lowering sea level and general climatic conditions.

Some secondary parameters may be involved in the Sr/Mg distribution. For instance, it is notable that the concentration of Mg in the skeletons from sample 59 (argillaceous chalk) cannot be compared with the extremely high content in the bulk sample. The high Mg content in the argillaceous horizons most likely is due to ion-exchange processes of the clay minerals. It is considered that the most abundant clay mineral in the chalk is montmorillonite (Christensen et al., 1973), which is remarkable for its very large exchange capacity.

Although  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$  are almost equally exchangeable, it appears from the present data that only Mg is correlated to the clay content (figs 2-3). This phenomenon is most likely caused by the much higher concentration of  $\text{Mg}^{2+}$  in pore solution, which favours the exchange by that cation (Grim, 1968).

By considering an extensive lowering of the sea level, the question of presence or absence of calcareous algae must be taken in account. The presence of magnesian calcite secreting algae probably could explain an increase in the Mg content in the sediments especially in the bryozoan limestone. However, at present no remains of calcareous algae have been detected in the numerous samples investigated. Furthermore, a significant increase of magnesian calcite caused by the presence of calcareous algae would certainly be reflected in more advanced diagenesis in the sediment than is actually observed. Proof of the presence of calcareous algae in the studied sediments is therefore lacking.

However, it must be considered that the observations concerning the relationship between bulk samples, carbonate skeletons and clay minerals are rather few and the interpretations only suggestive. Further research is required on the total Mg and Sr budget of the carbonate sediment.

## Conclusions

The chalk and the bryozoan limestone represent two essentially different biofacies in the section studied. While the bryozoan limestone has a rather homogeneous composition, the chalk is divided into white chalk, argillaceous chalk and hardground facies.

The white chalk, the argillaceous chalk and the bryozoan limestone have been influenced by an extremely uniform diagenesis dominated by pressure-solution processes. Only the sediments in the hardground horizon have undergone a complete alteration, resulting in cementation, partial dissolution of skeletal material and a thorough recrystallization of cement, the remaining skeletons and the micritic matrix.

By stressing the uniform diagenesis it is believed that the present recorded distribution of Mg and Sr at least relatively reflects the original content of those two elements incorporated into the carbonate fraction of the sediments.

The Sr and Mg distribution allows the establishment of 3 zones which most likely reflect the late Maastrichtian regression and the shift in biofacies at the Maastrichtian/Danian transition. The Sr/Mg distribution depends primarily on the original calcite/aronite ratio of the sediment, a feature which is well illustrated by the abrupt decrease of the Sr/Mg ratio at the transition from chalk to bryozoan limestone. The negative correlation between Mg and Sr is pronounced in the chalk sequence and is most likely the result of the temperature-dependent incorporation of the two elements into biogenic carbonates.

The decrease of the Sr/Mg ratio up through the chalk sequence is thus taken to be a result of an environmental temperature rise due to combination of lowering sea level and general climatic conditions in late Maastrichtian. There is also indication for a decreasing number of aragonitic contributors up through the section studied.

Ion-exchange processes related to the activity of the clay minerals present are believed to have had great influence on the local concentration and oscillation of the Mg. In contrast, the Sr is not affected by those processes, probably due to the low concentration of that cation in the interstitial pore fluid.

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## Dansk sammendrag

Kalksedimenterne i Maastrichtian/Danian grænseprofilen i Dania Kalkbrud er beskrevet med særlig vægt på Sr/Mg indholdet og diagenetiske processer. Maastrichtian sedimenterne består hovedsagelig af skrivekridt med flintlag og indtil flere lerede horisonter. Skrivekridtet afsluttes med en kalkhærdet bæk, hardground, som er gennemsat af utallige gravegange. Den kalkhærdede horisont overlejres af horisontalt beliggende bænke af bryozokalk fra Danian.

De undersøgte sedimentter er primært opbygget af biogene komponenter. De er velsorterede og domineret af kornstørrelser i silt-ler fraktionen. Med undtagelse af den kalkhærdede bæk er der ingen steder i profillet indikatorer for tilstedeværelsen af kemisk udfældet karbonat. Indholdet af terrigent materiale er ringe, men dog væsentligt større og varierende end almindelig set i det danske skrivekridt.

Skrivekridtet såvel som bryozokalken er kun svagt påvirket af diagenetiske processer. "Pressure-solution" synes at være mest almindelig forekommende, hvilket bl. a. har ført til konsolideringen af sedimentterne. Kun den kalkhærdede bæk er karakteriseret af mere komplicerede diagenetiske forhold.

Det understreges, at den meget ensartede diagenetiske påvirkning af de undersøgte sedimentter, har gjort det muligt at drage videregående slutninger på grundlag af Sr/Mg indholdet. Fordelingen af Mg og Sr er karakteriseret ved en tydelig negativ korrelation mellem de to elementer, der kommer til udtryk ved stigende Mg- og faldende Sr indhold op gennem lagserien. Mg indholdet varierer fra 1300 ppm til 4300 ppm, mens Sr indholdet er i størrelsesordenen 450-1100 ppm. Den negative korrelation mellem Sr og Mg er i overensstemmelse med opnåede resultater fra andre Maastrichtian/Danian lokaliteter i Danmark (Stevns Klint, Kjølbygaard, Erslev og Nye Kløv). Det undersøgte profil i Dania kan opdeles i 3 zoner på grundlag af Sr/Mg indholdet. Det pludselige fald i Sr/Mg forholdet på grænsen mellem Maastrichtian og Danian sættes i forbindelse med ændringen af biofacies på dette sted i lagserien. Derimod synes den jævne aftagen i Sr/Mg forholdet i skrivekridtet at skyldes en mindre temperaturstigning i Maastrichtian-havet, muligvis som resultat af aftagende vanddybde og klimatiske faktorer.

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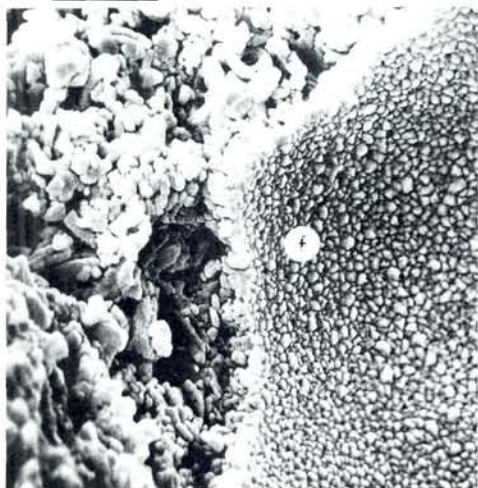
Figs 9-14. Fig. 9. Fracture surface of white chalk showing coccoliths enveloped by micritic matrix. (SEM). Fig. 10. Etched fracture surface of white chalk showing the prominent appearance of coccoliths and coccolith fragments enveloped by micritic matrix. (SEM). Fig. 11. Fracture surface of white chalk showing broken foraminiferal chamber wall (f), coccoliths and micritic matrix. Note the syntaxial growth of cement on the inner surface of the foraminiferal test. (SEM). Fig. 12. Fracture surface of white chalk showing coccolith (c), floating calcite crystal (fc) and lepidospheres (ls). (SEM). Fig. 13. Fracture surface of white chalk showing test of planktic foraminifera (f) enveloped by coccoliths and micritic matrix. (SEM). Fig. 14. Fracture surface of argillaceous chalk showing broken test of planktic foraminifera (f) enveloped by coccoliths and micrite matrix. Note the syntaxial growth of calcite cement on the inner surface of the foraminiferal test. (SEM).



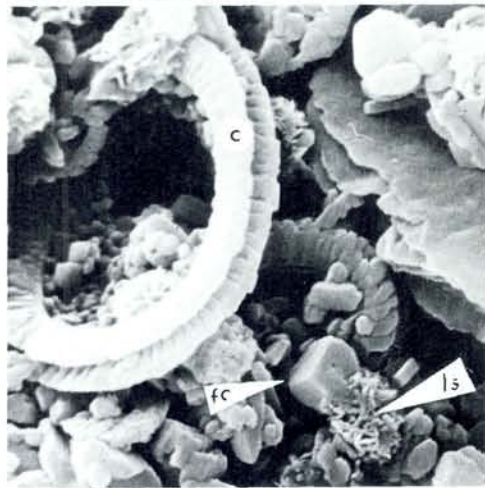
9 5  $\mu$ m



10 5  $\mu$ m



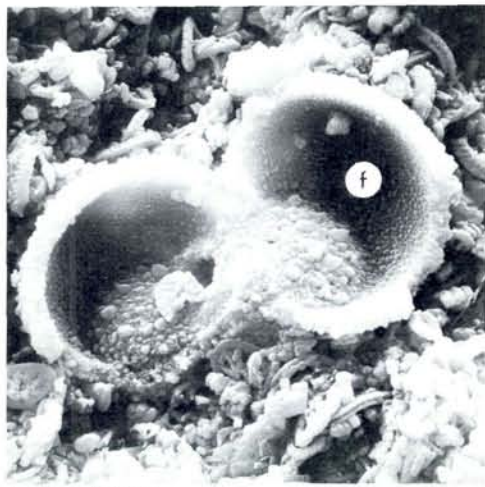
11 8  $\mu$ m



12 3  $\mu$ m



13 20  $\mu$ m



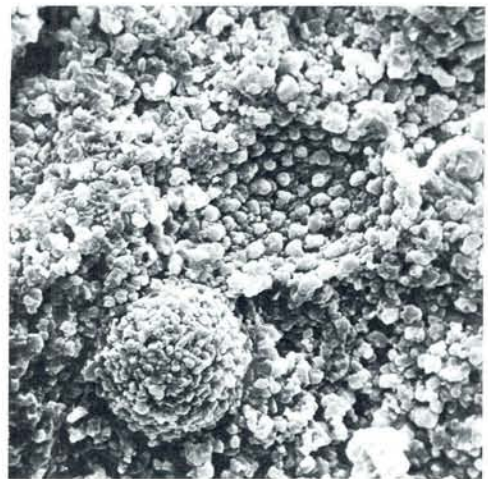
14 10  $\mu$ m

*Figs 15–20. Fig. 15. Fracture surface of argillaceous chalk showing abundant coccoliths, coccolith fragments and lepidospheres (ls). (SEM). Fig. 16. Fracture surface of the indurated limestone of the hardground showing internal and external moulds of presumably a foraminiferal test. Note the uniform grain size of the micritic matrix. (SEM). Fig. 17. Etched fracture surface of the indurated limestone of the hardground showing void-filling calcite cement (vc), and matrix. (SEM). Fig. 18. Etched fracture surface of the indurated limestone of the hardground showing void-filling calcite cement (vc), recrystallized foraminiferal chamber wall (f) and matrix. (SEM). Fig. 19. Two-stage replica of polished and etched section of the indurated limestone of the hardground showing skeletal fragment (sk) enveloped by matrix. Note the irregular interface between the oriented crystals of the skeleton and the grains of the matrix. At lower left is seen an infilling of calcite cement of a calcisphere. (TEM). Fig. 20. Two-stage replica of polished and etched section of indurated limestone of the hardground showing the equal grain size distribution and the irregular shape of the individual grains of the micritic matrix. (TEM).*

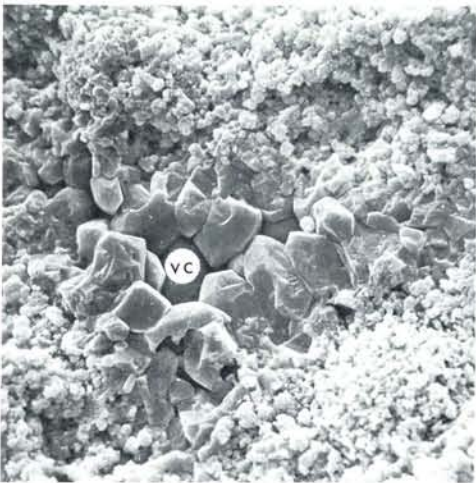




15 10 μm



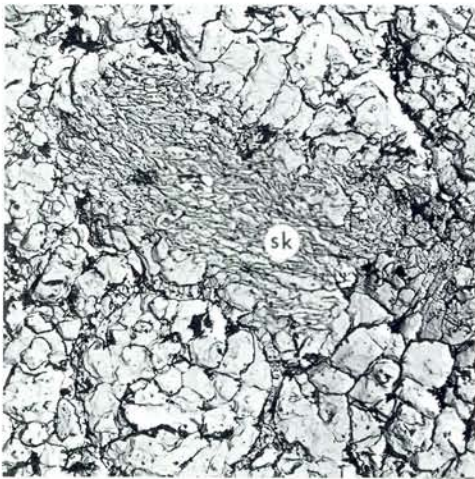
16 20 μm



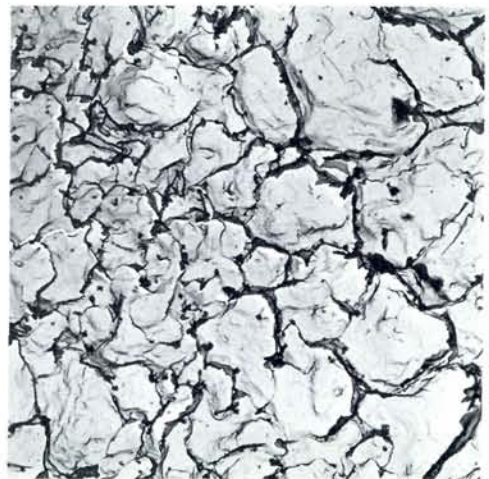
17 20 μm



18 20 μm



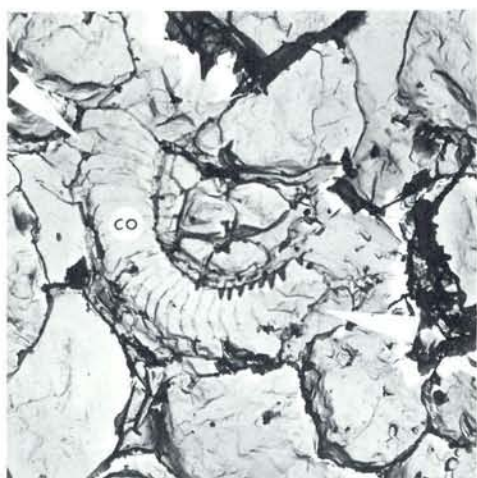
19 15 μm



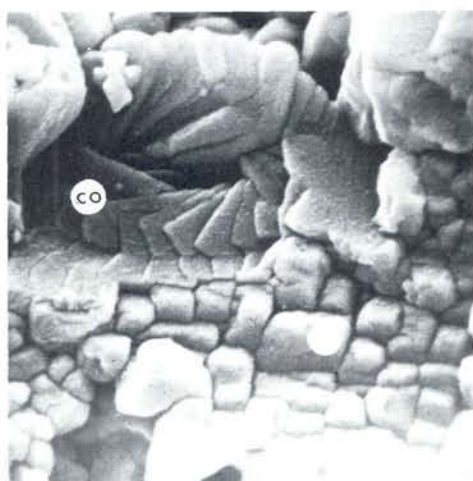
20 3 μm

*Figs 21–26. Fig. 21. Two-stage replica of polished and etched section of the indurated limestone of the hardground showing coccolith (c) partially displaced by the micritic matrix (arrows). (TEM). Fig. 22. Fracture surface of the indurated limestone of the hardground showing coccolith (c) partially displaced by oriented crystal growth of calcite cement (cc). (SEM). Fig. 23. Fracture surface of the indurated limestone of the hardground showing micritic matrix with locally developed crystal faces (arrows), but most commonly exhibiting irregular shape of the individual grain. (SEM). Fig. 24. Fracture surface of the partially indurated limestone from the lower part of the hardground showing well-preserved coccoliths and euhedral crystals of interstitial calcite cement (arrows). (SEM). Fig. 25. Fracture surface of the partially indurated limestone from the lower part of the hardground showing euhedral crystals of interstitial calcite cement. Note the inclusions of minute carbonate grains into the euhedral crystals (arrows). (SEM). Fig. 26. Fracture surface of partially indurated limestone from the lower part of the hardground showing cluster of euhedral calcite crystals with inclusions of minute carbonate grains (arrows). (SEM).*

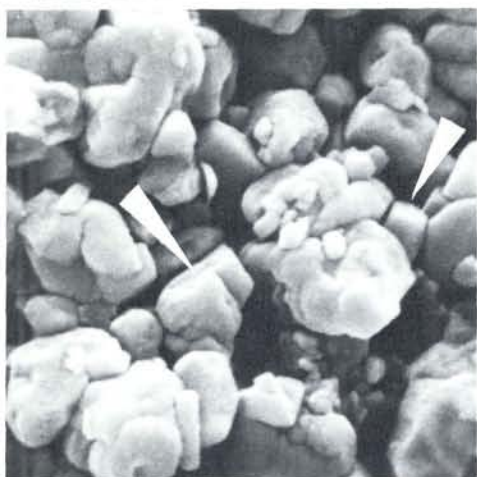




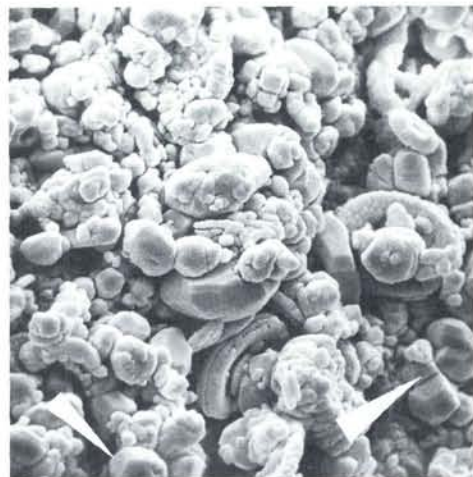
21  $2\mu\text{m}$



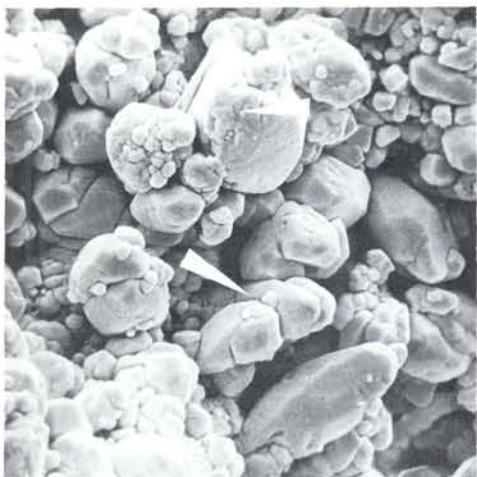
22  $2\mu\text{m}$



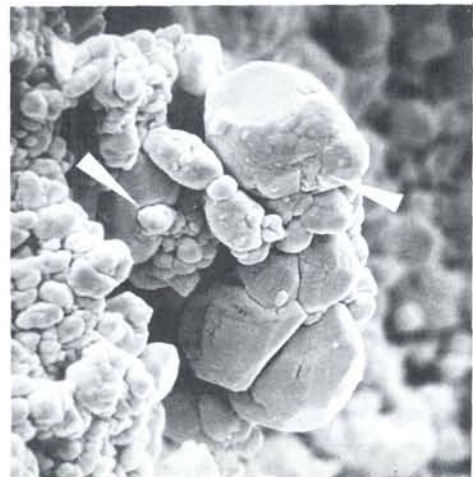
23  $2\mu\text{m}$



24  $10\mu\text{m}$

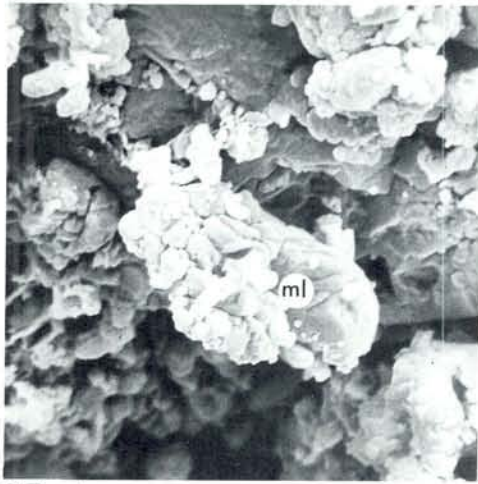


25  $5\mu\text{m}$



26  $5\mu\text{m}$

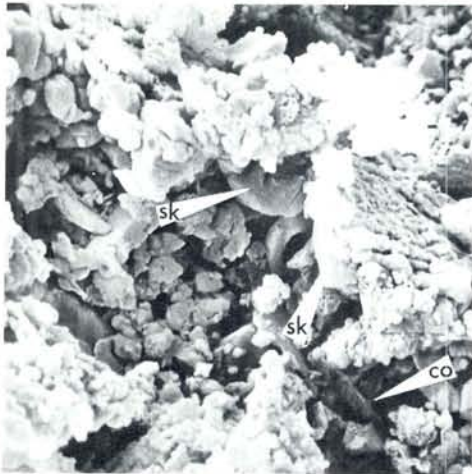
*Figs 27–32. Fig. 27. Fracture surface of bryozoan limestone showing microlumps (ml). (SEM). Fig. 28. Fracture surface of bryozoan limestone showing skeletal fragments (arrows) partially overgrown by syntaxial calcite cement. (SEM). Fig. 29. Fracture surface of bryozoan limestone showing skeletal fragments (arrows) and coccoliths (c). (SEM). Fig. 30. Fracture surface of bryozoan limestone showing skeletal fragments enveloped by micritic matrix. (SEM). Fig. 31. Fracture surface of bryozoan limestone showing recrystallized skeletal wall (sk). Note the abundant lepidospheres (arrows). (SEM). Fig. 32. Detail from fracture surface of bryozoan limestone showing syntaxial growth of calcite cement on the inner surface of bryozoan zoarium. (SEM).*



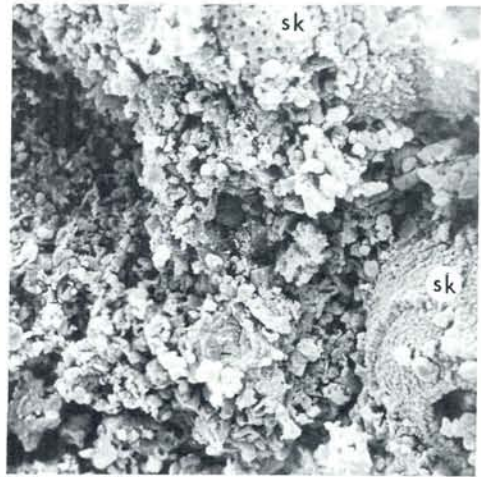
27  $6 \mu\text{m}$



28  $10 \mu\text{m}$



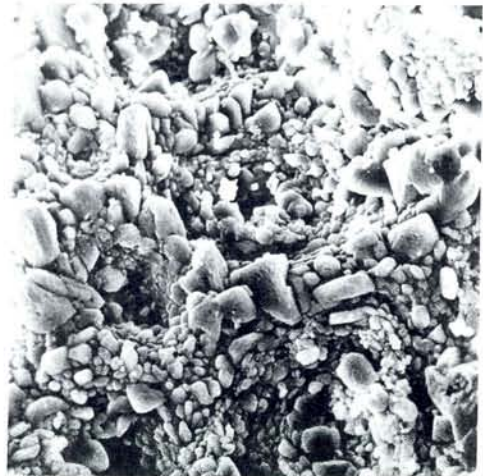
29  $5 \mu\text{m}$



30  $20 \mu\text{m}$



31  $10 \mu\text{m}$



32  $40 \mu\text{m}$